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FINAL REPORT CONCERNING THE SOLUBILITY OF OXYGEN IN SULFURIC ACID-ZINC PRESSURE LEACHING SOLUTIONS

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CONTENTS

1.0	SUMMARY	1
2.0	INTRODUCTION	3
3.0	EXPERIMENTAL EQUIPMENT AND PROCEDURE	4
	3.1 For solubility measurements	4
	3.2 For density measurements	9
4.0	RESULTS AND DISCUSSION	11
	4.1 For solubility measurements	11
	4.2 Models for oxygen solubility	18
	4.3 For density measurements	21
	4.4 Models for densities of solutions	21
	4.5 Oxygen solubility in Cominco autoclave effluent and in sample containing Lignosol	24
5.0	CONCLUSIONS	29
6.0	REFERENCES	30
7.0	APPENDIX A: Vapor pressures of aqueous sulfuric acid, zinc and iron sulfate solutions	31
8.0	APPENDIX B: Equations obtained for expressing solution density as a function of acid, zinc and iron concentrations	34
9.0	APPENDIX C: Analysis of Cominco autoclave effluent sample	35
10.0	APPENDIX D: Equations used for calculating solubility	36

TABLES

TABLE I	Solubility of oxygen in synthetic sulfuric acid leach solutions for an oxygen partial pressure of one atmosphere	13
TABLE II	Densities and molar concentrations of test solutions	22
TABLE III	Oxygen solubility in solution containing Lignosol and in a Cominco autoclave effluent sample	27
TABLE IV	Vapor pressures of aqueous solutions of sulfuric acid, zinc and iron sulfate salts	33

FIGURES

FIGURE 1	Apparatus for the determination of oxygen solubility at high temperatures: High Pressure Solubility Apparatus	7
FIGURE 2	Effect of pressure on oxygen solubility in test solutions at 95°C: Mole Fraction Solubility of Oxygen in Aqueous Sulfuric Acid Solutions	12
FIGURE 3	Oxygen solubility in test solutions expressed as the mole fraction for a partial pressure of 101.3 kPa	16
FIGURE 4	Oxygen solubility in test solutions expressed in g/L for a partial pressure of 101.3 kPa	17
FIGURE 5	Effect of sulfuric acid, dissolved zinc and iron on solubility of oxygen at 95°C	19
FIGURE 6	Effect of sulfuric acid, dissolved zinc and iron on density of solutions at 155°C	23

1.0 SUMMARY

Solubilities of oxygen were measured at four temperatures (95°C, 125°C, 155°C and 185°C), for three partial pressures of oxygen (4 atm, 7atm and 10 atm),and for aqueous sulfuric acid solutions containing zinc and iron sulfate salts. Because of the high vapor pressure of the solutions at 185°C and the equipment limitations at pressures exceeding 300 psig, the three oxygen pressures chosen for the solubility determinations at that temperature were 7 atm, 4 atm and 2 atm. Some of the solution compositions are similar to those used in the pressure leaching process for the recovery of zinc.

The solubility data indicated that Henry's law was followed for all the solutions tested. Thus, a single average value of solubility is reported corresponding to an oxygen partial pressure of 101.3 kPa (one atmosphere) for each solution at each temperature.

A two-stage process for solubility determinations, consisting of a high pressure, high temperature absorption step and a low pressure (atmospheric) desorption step at 50°C, was developed. It was therefore, necessary to measure the oxygen solubilities in the various solutions at 50°C and atmospheric pressure. These data are also reported.

In addition, the solubilities of oxygen were measured in two special solutions consisting of a concentrated zinc sulfate solution containing a specified amount, 0.3 g/L of surfactant Lignosol, as well as the industrial sample obtained from the pressure leaching unit of Cominco at Trail, British Columbia, in May, 1990. Oxygen solubilities were measured in the former solution at 125°C for oxygen pressures of 10 atm, 7 atm and 4 atm. The solubility of oxygen from <u>air</u> at air pressures of 10

atm, 7 atm and 4 atm was also determined at a temperature of 155°C. For the Cominco sample, oxygen solubilities from air were also determined for the same three air pressures and for a temperature of 155°C. These data are reported.

Solution densities were measured and are reported for all the solutions used for six temperatures from 25°C to 185°C. Of necessity, dilatometer tubes, pressurized with oxygen, were used for the density determinations for temperatures from 95°C to 185°C. A densitometer was used for the low temperature measurements.

Models were developed expressing the effects of solution composition for aqueous sulfuric acid as well as of zinc and iron sulfate salts on the oxygen solubility and solution density. These models show that there is a systematic effect of the concentration of each of the three components on oxygen solubility in aqueous solutions as well as on solution density.

In this report the concentrations of the components in the solutions will be represented in g/L as in the following example: 5/110/1, the first number representing g/L of sulfuric acid, the second number representing g/L of divalent zinc and the third number prepresenting g/L of ferric or trivalent iron in the aqueous solutions. Further, in describing the solutions, the term "acid" will represent sulfuric acid, "zinc" will represent divalent zinc in solution and "iron" will represent ferric or trivalent iron in solution. The actual solutions were prepared from hydrated zinc and ferric iron sulfate salts in quantities sufficient to give the indicated masses of dissolved metals.

2.0 INTRODUCTION

This investigation was initiated by Dr. J.E. Dutrizac and Dr. K.G. Tan of the Department of Energy Mines and Resources. The purpose was to provide a systematic study of oxygen equilibrium data which may be useful in the analysis of the pressure leaching process for the recovery of zinc from sulfide concentrates. The main part of this work has been presented as an M.A.Sc. thesis in the Chemical Engineering Department of the University of Ottawa (Kimweri, 1990).

Few data appear in the literature for the solubility of oxygen in water at temperatures above 100°C and even fewer for the solubility in aqueous sulfuric acid. These latter data were generally obtained early in the century and are not considered to be reliable. No data have been found for the solubility of oxygen in aqueous sulfuric acid-zinc sulfate solutions. Hence most of this work is a new addition to the technical literature. A discussion concerning the solubility of oxygen in water, in aqueous sulfuric acid and in some aqueous salt solutions is found in the volume published by IUPAC (Battino, 1981).

3.0 EXPERIMENTAL EQUIPMENT AND PROCEDURE

3.1 For solubility measurements

A two-stage method for measuring the high pressure solubilities was used. First, oxygen was absorbed at constant temperature and pressure in a high pressure absorber at an oxygen partial pressure of 10 atm using deaerated solvent. Next, when saturation was complete, a stream of the saturated solution was directed through a needle valve to a glass desorption apparatus operated at atmospheric pressure and at 50°C. It was found that equilibrium conditions were easier to achieve in the high pressure absorber by initially starting at the highest partial pressure of oxygen (10 atm), and subsequently by reducing the oxygen pressure to 7 atm and then to 4 atm. It was found that a shorter time was required to achieve saturation from an initially supersaturated condition than that required to equilibrate from an unsaturated solution.

The high pressure absorption apparatus consisted of a stainless steel pressure vessel having a solvent capacity of about 600 ml, equipped with a Pyrex glass insert or liner to contain the solvent. The purpose of the Pyrex glass vessel was to prevent corrosion of the stainless steel by the sulfuric acid solutions at the high temperatures. A magnetic stirrer inside the Pyrex vessel could be operated even though the pressure vessel was immersed in an oil bath.

After an initial charging and heating period, the acid solvent was deaerated by intermittently purging some of the steam from the heated absorption vessel to an ice-cooled trap. The volume of water evaporated in the process of deaeration amounted to 3-8 ml. Thus the small increase in acid or metal salt concentration as a result of deaeration was

considered to have a negligible effect on the oxygen solubility.

It was observed that the stainless steel tube immersed in the hot sulfuric acid solutions became corroded at 185°C even though it was protected on the outside with a Teflon sleeve. The corrosion was especially severe when the solutions contained no iron salt. Not only was the tube corroded but some gas (probably hydrogen) was also evolved when the hot solution was passed through it, thus interfering with the volumetric determination of oxygen. Therefore, an attempt was made to use titanium tubing for supplying the hot acid solution to the desorption apparatus. It was found, however, that the solutions containing no iron still corroded the titanium tube at 185°C. Advice was received from Dr. E. Peters, Professor of Metallurgical Process Engineering at U.B.C., concerning this problem. He indicated that ferric ion (or other oxidized ions) must be present in a hot sulfuric acid solution to passivate the titanium, and recommended that a concentration of 2 g/L of ferric ion be used. For that reason a level of 2 g/L of ferric iron was used in the three solutions originally specified to contain no iron for the temperature of 185°C.

It is noted that solubilities of oxygen were measured in solutions containing acid, zinc and iron in the proportions 5, 110, 0 and 5, 110, 1 g/L. The addition of 1 g/L of iron in the latter solution produced only a small change in the oxygen solubility. A quantitative estimate of the effect of the addition of 2 g/L of ferric iron is available by comparing the solubility results for the solutions containing 60, 75, 0 and the 60,75,10 g/L acid, zinc and iron. The effect of the 10 g/L of added iron is a 6% decrease in oxygen solubility at 185°C. This corresponds to a 1.2% decrease in oxygen solubility for an addition of 2 g/L of iron. The measured oxygen solubility was adjusted to compensate for the presence of

the added iron sulfate in these solutions.

The quantity of dissolved oxygen contained in the acid solutions saturated at higher pressures and temperatures was determined in a glass desorption apparatus operated at atmospheric pressure and at 50°C. The glass desorption apparatus consisted of a spiral coil through which the supersaturated solvent flowed as a thin film, releasing oxygen. The coil was connected at the top to a burette, initially filled with mercury, and at the bottom to a small U-tube manometer through which the solvent flowed and which acted as a seal, confining the gas in the spiral coil. The manometer also served as a pressure indicator by comparison with atmospheric pressure. Thus as the pressure gradually rose in the gas collecting system, the level of mercury was lowered in the burette. Because it was difficult to lower the mercury level steadily as the oxygen was evolved, a motorized screw device, driven by a variable-speed motor, was used for that purpose. The solvent was considered to be in equilibrium with the oxygen at the outlet of the desorption coil. The volume of gas was read directly from the gas burette and the volume of solvent was read using a graduated cylinder.

Details of the equipment are shown in Figure 1. Of special note are the use of a high precision transducer system for pressures readable to 0.01 psi and the temperature controller for the insulated constant temperature bath which maintained a temperature to within 0.1°C. It is further noted that for the sake of economy, safety and convenience, the bath oil was an edible peanut oil which could be used continuously at high temperatures for up to one month before some degradation occurred. The peanut oil became somewhat viscous after this time period and was replaced with fresh oil. The high pressure part of the apparatus was mounted in a

HIGH PRESSURE SOLUBILITY APPARATUS

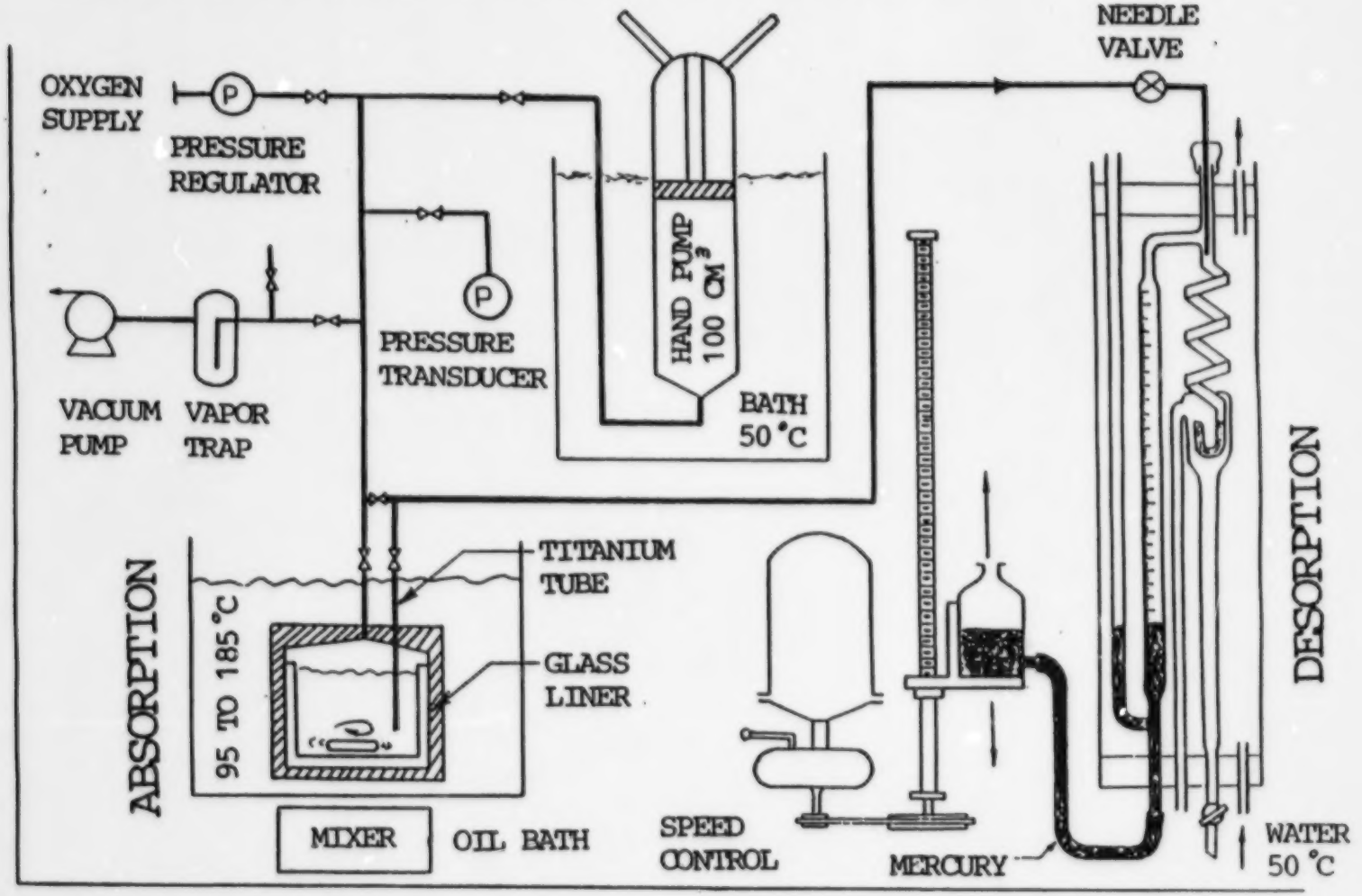

Fig. 1

fume hood.

One experiment consisted of charging the high pressure absorption vessel, sealing the top of the vessel with a Teflon gasket and placing the vessel into the constant temperature bath. After deaeration, the absorption vessel was pressurized with oxygen to a pressure equivalent to an oxygen partial pressure of 10 atmospheres, and was equilibrated for several hours. A final adjustment in pressure was made and the equilibration continued over night. The next morning, about 75 ml of the saturated solution was slowly transferred to the desorption apparatus while maintaining a constant pressure in the high pressure vessel. About 15 pairs of readings of oxygen volume at atmospheric pressure and solvent volume were collected for each desorption run. Next, the oxygen pressure was reduced to an oxygen pressure of 7 atm. An equilibration period of 2-3 hours was required before a second solubility determination was made at the lower pressure. This procedure was repeated again at an oxygen partial pressure of 4 atm. The pressure vessel was then removed and recharged for the next solubility determination.

Only a minor change in procedure was required for solubility determinations using compressed air. During the desorption step of the procedure, the desorbed gas was accumulated in the gas burette at 50°C and atmospheric pressure. Using a syringe, a sample of the accumulated gas was withdrawn for analysis by gas chromatography (GC). In this way it was possible to determine the composition and, hence, the partial pressure of oxygen in the gas phase as well as to determine the quantity of oxygen released during desorption. The total quantity of oxygen dissolved at high pressure was calculated as the sum of that desorbed in the gas at low pressure and that still remaining in solution at 50°C and atmospheric

pressure.

3.2 For density measurements

The densities of the solutions were measured by two entirely different methods, one involving a digital vibrating-reed densitometer which was used at 25°C and 50°C. At the higher temperatures, the densitometer could not be safely used because of the corrosiveness of the acid solution and the temperature limitations of the equipment. For the higher temperatures, four dilatometer tubes constructed of thick-walled Pyrex glass capillary tubing of about 60 cm length and having an internal diameter of about 1 mm were used. One end was sealed by glass blowing while the other end was flared and joined to a stainless steel fitting using a Teflon ferrule. The tubes were also bent at a 90° angle so that they could be almost totally immersed in the oil bath.

The use of the dilatometer tubes involved charging the deaerated solutions into the tubes using a syringe equipped with a long flexible needle so that no air became trapped in the column of liquid. The tubes were filled with the different solutions to within 6 cm of the top ends allowing for the relatively large expansion of the solutions with increasing temperature. Before measurements were begun, the tubes were pressurized with oxygen to prevent boiling and were heated to 50°C as an initial temperature. The dilation or expansion was accurately measured using a cathetometer which was used to locate the position of the gas-liquid interface inside the dilatometer to within 0.02 mm. When thermal equilibrium was attained at the temperatures of 95°C, 125°C, 155°C and 185°C in succession, the expanded liquid level readings were obtained. In each case, the dilation of the solution was at least 0.7 cm and, along with a knowledge of the total length of the solution in

the tubes, enabled a calculation of solution densities.

Distilled water was used to determine the small correction factor which accounted for the minor expansion of the Pyrex glass and for the small amount of evaporation on heating the solutions. The densities of four solutions were measured at all four temperatures as part of one experiment. The long dilatometer tubes tended to operate in a manner similar to thermometers and gave consistent results relatively quickly. The major difficulty was in providing a suitable sealing method between the glass and the stainless steel.

The low temperature density measurements were relatively simple. The vibrating frequency of an electronically vibrated reed is closely related to the density of the fluid in which it is immersed. The frequency of vibration is measured electronically and displayed. Thus the instrument is calibrated with two fluids of known density, distilled water and ethylene glycol in this case, and then used directly to measure the densities of solutions filling the small density tube containing the vibrating reed. The instrument used was from Anton Paar (Austria) and was highly accurate. Because of the internal sealing and electronic sensing materials, however, it could not be used at high temperatures or with corrosive fluids.

4.0 RESULTS AND DISCUSSION

4.1 For solubility measurements

Typical results for oxygen solubilities in the synthetic acid solutions at the three pressures 10, 7 and 4 atmospheres of oxygen are shown for a temperature of 95°C in Figure 2. It is apparent from Figure 2 that the solubility behavior of these solutions closely conforms to Henry's law at 95°C in that the solubility increases directly with increasing pressure. Similar behavior was observed at the other temperatures. Further, Figure 2 clearly shows the very large reduction in oxygen solubility in the aqueous acid solutions containing high zinc concentrations. For the solution containing 110 g/L of zinc, the oxygen solubility is only about 40% of that in water or dilute (5 g/L) acid. There are also reductions in oxygen solubilities as a result of increasing acid concentrations and of increasing iron concentrations in the solutions.

Computer calculations were employed to calculate the mole fraction solubility, Henry's law constant, solubility expressed in g/L and the Bunsen coefficient (volume of oxygen at STP per volume of solvent). Also calculated was an average Henry's law constant and average gas solubility corresponding to an oxygen partial pressure of one atmosphere, for each solution at each temperature. At least two determinations were made at each different condition and concentration. Especially at the higher temperatures (155°C and 185°C), additional replicate determinations were made because there was some difficulty in obtaining highly consistent results.

The average oxygen solubility results are reported for a gas partial pressure of one atmosphere in Table 1. Using Henry's law, solubilities at

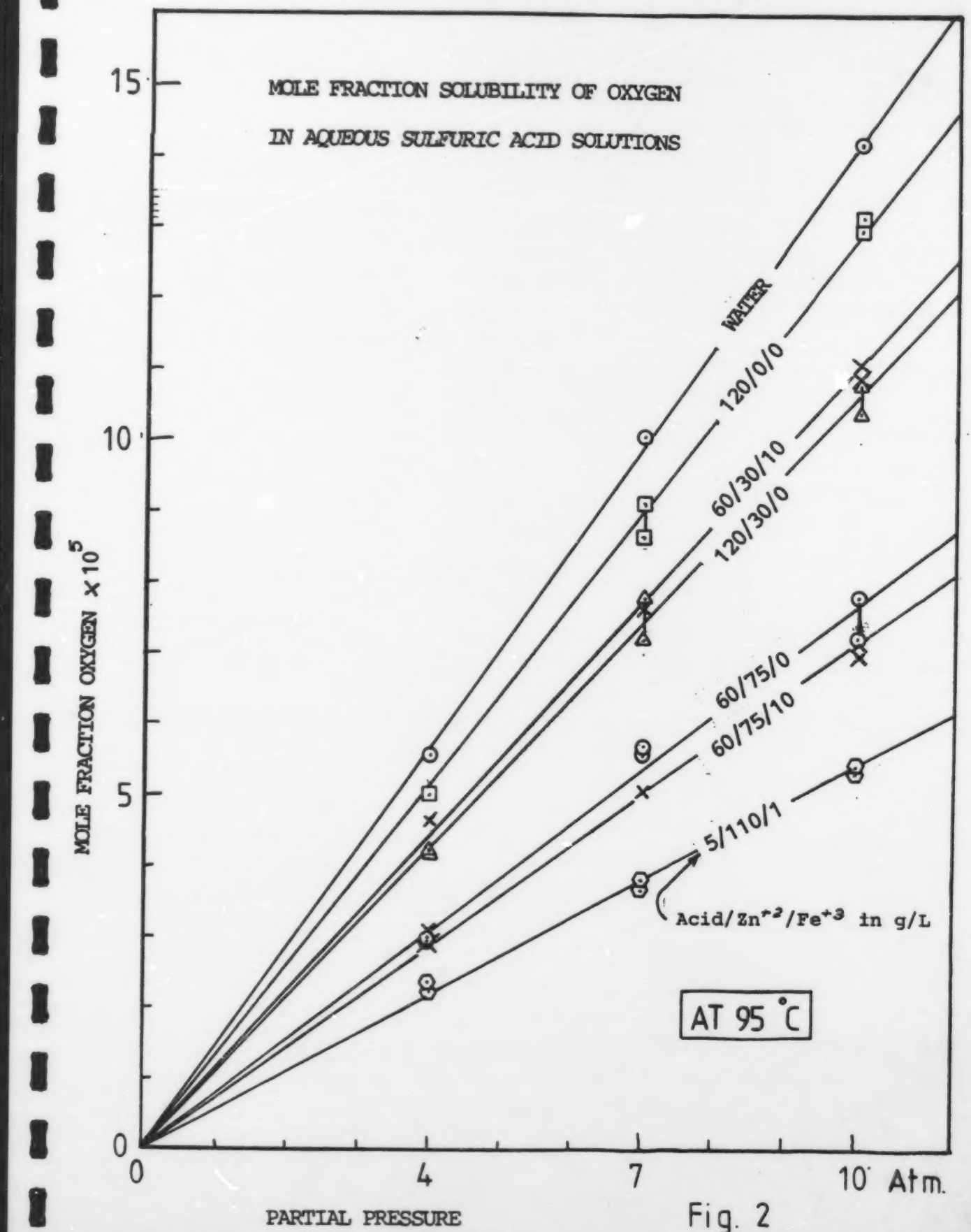
MOLE FRACTION SOLUBILITY OF OXYGEN
IN AQUEOUS SULFURIC ACID SOLUTIONS
MOLE FRACTION OXYGEN x 10^5
15
10
5
0
WATER
120/0/0
60/30/10
120/30/0
60/75/0
60/75/10
5/110/1
Acid/Zn+2/Fe+3 in g/L
AT 95 °C
0
4
7
10 Atm.
PARTIAL PRESSURE

Fig. 2

TABLE I SOLUBILITY OF OXYGEN IN SYNTHETIC SULFURIC ACID LEACH SOLUTIONS FOR AN OXYGEN PARTIAL PRESSURE OF ONE ATMOSPHERE

Composition	Temp. °C	50	95	125	155	185
120/0/0	s	0.0235	0.0212	0.0227	0.0265	0.0325
	$(10^5)x$	1.38	1.27	1.40	1.67	2.11
	$(10^{-3})H$	72.5	78.7	71.4	59.9	47.4
	β	0.0165	0.0148	0.0159	0.0186	0.0228
120/30/0	s	0.0193	0.0175	0.0189	0.0224	0.0285
	$(10^5)x$	1.13	1.05	1.16	1.41	1.84
	$(10^{-3})H$	88.5	95.2	86.2	70.9	54.3
	β	0.0135	0.0123	0.0132	0.0157	0.0200
60/30/10	s	0.0189	0.0172	0.0186	0.0218	0.0277
	$(10^5)x$	1.10	1.03	1.14	1.37	1.79
	$(10^{-3})H$	90.9	97.1	87.7	73.0	55.9
	β	0.0132	0.0121	0.0130	0.0153	0.0194
60/75/0	s	0.0147	0.0131	0.0143	0.0177	0.0241
	$(10^5)x$	0.84	0.77	0.86	1.09	1.53
	$(10^{-3})H$	119	130	116	91.7	65.4
	β	0.0103	0.0092	0.0100	0.0124	0.0169
60/75/10	s	0.0133	0.0119	0.0133	0.0166	0.0225
	$(10^5)x$	0.76	0.70	0.80	1.02	1.43
	$(10^{-3})H$	132	143	125	98	69.9
	β	0.0093	0.0083	0.0093	0.0116	0.0158

continued...

TABLE I ...CONTINUED

Composition	Temp. °C	50	95	125	155	185
5/110/1	s	0.0111	0.0093	0.0106	0.0146	0.0209
	$(10^5)x$	0.62	0.53	0.62	0.88	1.30
	$(10^{-3})H$	161	189	161	114	76.9
	β	0.0078	0.0065	0.0074	0.0102	0.0146
water	s	0.0298	0.0243	0.0260	0.0298	0.0358
	$(10^5)x$	1.70	1.42	1.56	1.84	2.29
	$(10^{-3})H$	58.8	70.4	64.1	54.3	43.7
	β	0.0209	0.0170	0.0182	0.0209	0.0251
5/0/0/	s	0.0294	0.0239	0.0257	0.0298	0.0356
	$(10^5)x$	1.68	1.40	1.54	1.84	2.27
	$(10^{-3})H$	59.5	71.4	64.9	54.3	44.1
	β	0.0206	0.0167	0.0180	0.0209	0.0249
5/110/0	s	0.0113	0.0095	0.0109	0.0150	0.0217
	$(10^5)x$	0.63	0.54	0.64	0.90	1.35
	$(10^{-3})H$	159	185	156	111	74.1
	β	0.0179	0.0066	0.0077	0.0105	0.0152

NOTE: Composition is in g/L of: acid/zinc/iron, respectively

s = g/L (g oxygen per L of solvent at indicated temperature)

x = mole fraction of oxygen, with the number of moles of dissolved acid and salts being considered

H = Henry's constant, atm/mole fraction

β = Bunsen coefficient, volume of oxygen at STP per volume of solvent or cm^3 (STP) $/cm^3$

other oxygen partial pressures can be determined as simple factors of the solubility at a partial pressure of one atmosphere. These data are also shown graphically in Figures 3, and 4, in which the mole fraction solubility, and oxygen solubility expressed in g/L, respectively, are shown. It may be observed that there is a minimum solubility of oxygen in water at about 95°C. Comparable minimum solubilities are also observed for the various leaching solutions.

It is useful to discuss some aspects of the solubility calculations. It was assumed that oxygen behaved as an ideal gas. This is known to be true to a fraction of a percent for the conditions used in these measurements. Next, Henry's law may be expressed as:

$$p = H\,x \qquad (1)$$

Then Henry's constant, H, is expressed in units of atm/mole fraction when p is expressed in atm, and is simply given by 1/x where the oxygen partial pressure is one atmosphere. In the calculation of the solubility in g/L, it is necessary to know the number of moles of acid and dissolved salts per litre of solution, as well as the solution density at each temperature. These values, of course, have been measured and are reported and discussed subsequently. The Bunsen coefficient is sometimes used as well as Henry's constant to describe the effect of pressure on gas solubility. The Bunsen coefficient, representing the volume of gas at STP dissolved in a unit volume of solvent, is also essentially constant with changing equilibrium pressure.

The accuracy of the solubility results was estimated. Solubility determinations using absorption methods alone may contain errors of up to

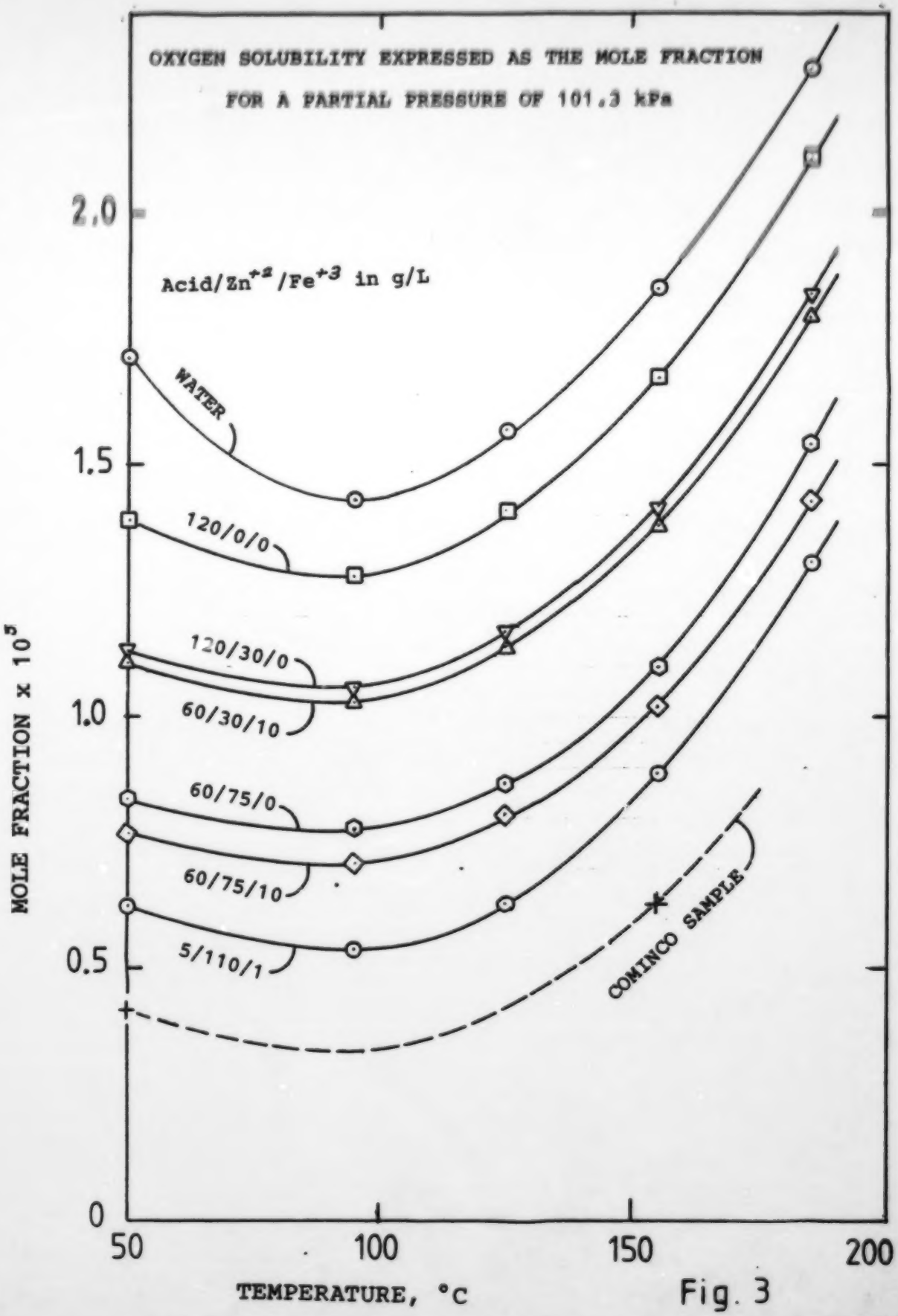
OXYGEN SOLUBILITY EXPRESSED AS THE MOLE FRACTION
FOR A PARTIAL PRESSURE OF 101.3 kPa
Acid/Zn+2/Fe+3 in g/L
WATER
120/0/0
120/30/0
60/30/10
60/75/0
60/75/10
5/110/1
COMINCO SAMPLE
MOLE FRACTION x 10^5
2.0
1.5
1.0
0.5
0
50
100
150
200
TEMPERATURE, °C

Fig. 3

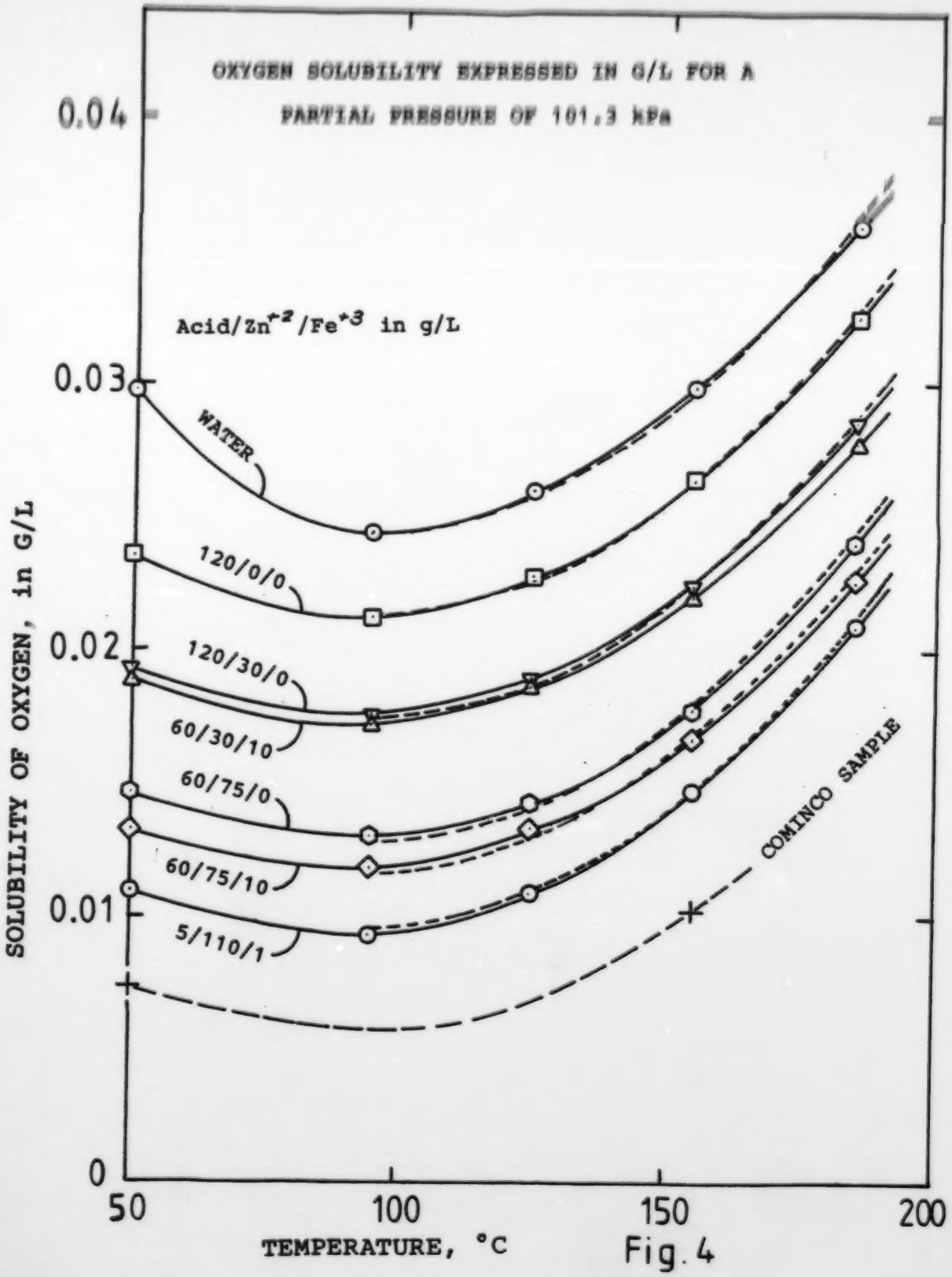
OXYGEN SOLUBILITY EXPRESSED IN G/L FOR A
PARTIAL PRESSURE OF 101.3 kPa
Acid/Zn+2/Fe+3 in g/L
WATER
120/0/0
120/30/0
60/30/10
60/75/0
60/75/10
5/110/1
COMINCO SAMPLE
SOLUBILITY OF OXYGEN, in G/L
0.04
0.03
0.02
0.01
0
50
100
150
200
TEMPERATURE, °C

Fig. 4

2%. In this case two consecutive operations are required for each determination: first an absorption step at high pressure, then a desorption step at low pressure. It is considered that the second step has a potential error of 2% as well. In consequence, the overall accuracy for most of the solubility results is estimated to be ± 4%. Finally, for the results involving the solubility of oxygen from air, yet a third step was involved, and that was an analysis by GC of the desorbed gas at atmospheric pressure from solutions saturated at higher pressures and temperatures. The uncertainty of the sampling and analysis procedure is also estimated at 2%. Thus the overall uncertainty of the results involving the solubility of oxygen from air is estimated to be ±6%.

4.2 Models for oxygen solubility in synthetic pressure leaching solutions

It is possible to represent the oxygen solubility data in water and the various solutions with approximate equations. From an observation of Figures 3 and 4, it is apparent that the nature of the temperature effect on solubility is basically parabolic in the temperature range from 95°C to 185°C. Not as apparent is the simple linear effect of increasing quantities of sulfuric acid, as well as of dissolved zinc and iron sulfates in reducing the oxygen solubilities by an amount proportional to the concentrations. These effects are indicated in Figure 5 which shows that increasing concentrations of sulfuric acid reduce the oxygen solubility in direct proportion to the acid concentration, albeit a relatively small amount. The effect of increasing concentrations of dissolved zinc is much greater than that of sulfuric acid. A large reduction in solubility is observed with 110 g/L of zinc in solution, for example. Similarly, although not investigated in detail, there is a

EFFECT OF SULFURIC ACID, DISSOLVED ZINC AND IRON ON SOLUBILITY OF OXYGEN AT 95°C

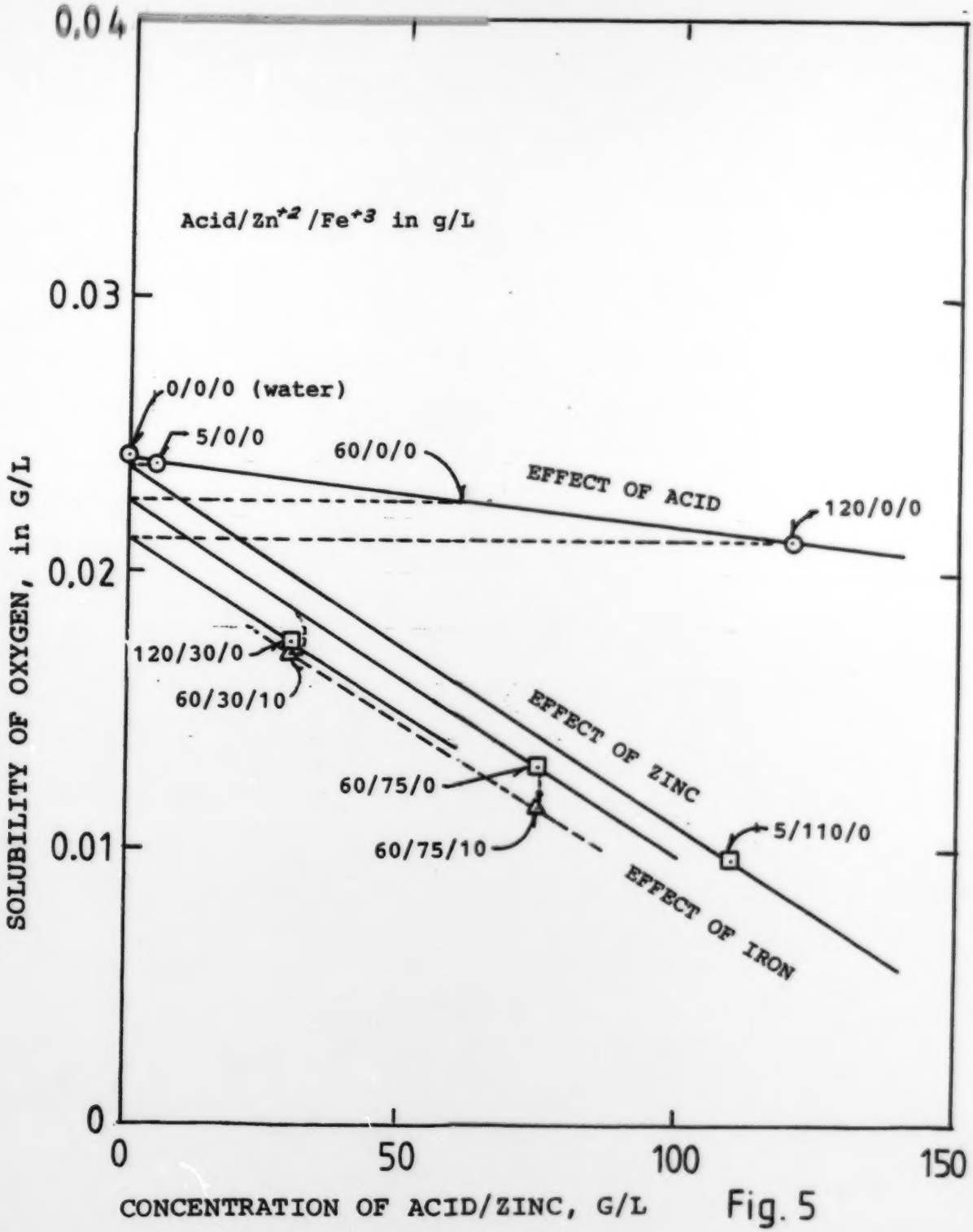

Fig. 5

further reduction in solubility as dissolved iron is added to the solution. Figure 5 is typical of the solubility behavior at the three other temperatures. It is also of considerable interest that quite closely, the effect of added acid, zinc or iron appears to be approximately the same at 95°C as at 125°C, 155°C and 185°C. Thus, it was possible to describe all the solubility data by a simple model with the oxygen solubility (s) and concentrations in solution of acid, zinc and iron (C_A, C_Z, C_I) all expressed in g/L.

For water alone, the parabolic equation is:

$$s = 0.0244 + (10^{-5})\ 0.144\ (T - 95)^2 \qquad (2)$$

For aqueous acid, a decrement proportional to acid concentration is introduced:

$$s = 0.0244 + (10^{-5})\ \{\ 0.144\ (T - 95)^2 - 2.60\ C_A\ \} \qquad (3)$$

For solutions containing dissolved acid, zinc and iron, further decrements are made:

$$s = 0.0244 + (10^{-5})\ \{\ 0.144\ (T - 95)^2 - 2.60\ C_A - 13.2\ C_Z - 15.0\ C_I\ \} \qquad (4)$$

The above equations were developed using a modelling procedure based on the data available and are only approximate because of the range of variables represented. The average absolute deviation of any one value from the measured results is 1.5% with deviations as high as 3% in some instances. However, considering the quantity of data represented by

Equation (4), the equation is considered very successful indeed. Also, it can be stated that there is a systematic effect of the dissolved salts on the oxygen solubility in these solutions. The dashed lines in Figure 3 indicate values calculated using Equation 4 which can be compared with the actual data (solid lines). Equation 4 is empirical and cannot be used with any degree of accuracy outside the temperature range 95°C to 185°C, nor outside the concentration range 0 to 120 g/L acid, 0 to 110 g/L of dissolved zinc or 0 to 10 g/L of dissolved iron. It should be a suitable model for interpolating solubilities to various temperatures and concentrations within the specified ranges, however.

4.3 For density measurements

The results of the density measurements for the various solutions are shown in Table II along with calculated values of the molar concentrations for the temperature range from 25°C to 185°C. In the concentration range of acid utilized here (0 to 120 g/L), the densities of the aqueous acid solutions are a linear function of acid content as tabled in the Chemical Engineers' Handbook. Furthermore, for each acid concentration, the densities of the solutions containing zinc increase linearly with zinc content. Similarly, solution densities containing dissolved iron indicate a further increase in density which is directly proportional to the iron content. These effects may be observed in Figure 6 which shows the densities of the various solutions and which is typical of the effects at the other temperatures.

4.4 Models for densities of solutions

For the range of temperatures (95°C to 185°C) and concentrations of acid (pure water to 120 g/L), zinc (0 - 110 g/L) and iron (0 to 10 g/L),

TABLE II DENSITIES AND MOLAR CONCENTRATIONS OF TEST SOLUTIONS

Composition	Temp.°C	25	50	95	125	155	185
120/0/0	d	1083	1068	1043	1017	993.4	965.5
	m	54.6	53.9	52.6	51.3	50.1	48.7
120/30/0	d	1142	1134	1107	1082	1055	1029
	m	56.7	56.3	55.0	53.7	52.4	51.1
60/30/10	d	1141	1123	1095	1069	1043	1014
	m	59.0	58.1	56.6	55.3	53.9	52.4
60/75/0	d	1206	1193	1164	1134	1107	1073
	m	61.2	60.5	59.1	57.5	56.2	54.4
60/75/10	d	1236	1224	1194	1165	1139	1104
	m	62.5	61.9	60.4	58.9	57.6	55.8
5/110/1	d	1261	1247	1220	1189	1159	1121
	m	65.3	64.6	63.2	61.6	60.0	58.0
water	d	997.1	988.0	961 9	939.1	912.3	881.6
	m	55.3	54.8	53.3	52.1	50.6	48.9
5/0/0	d	1001	991.8	966.7	943.9	918.2	887.9
	m	55.3	54.8	53.3	52.1	50.6	49.0
5/110/0	d	1256	1245	1217	1186	1155	1118
	m	65.0	64.4	63.0	61.4	59.8	57.8
5/110/1/0.3	d	-	1250	1221	1190	1160	1121
	m	-	64.6	63.2	61.6	60.0	58.0
Cominco	d	-	1383	1351	1318	1286	1249
	m	-	68.9	67.3	65.7	64.1	62.3

Note: d = density, kg/m^3 or g/L

m = molar concentration, mol/L

EFFECT OF SULFURIC ACID, DISSOLVED ZINC AND IRON ON DENSITY OF SOLUTIONS AT 155°C

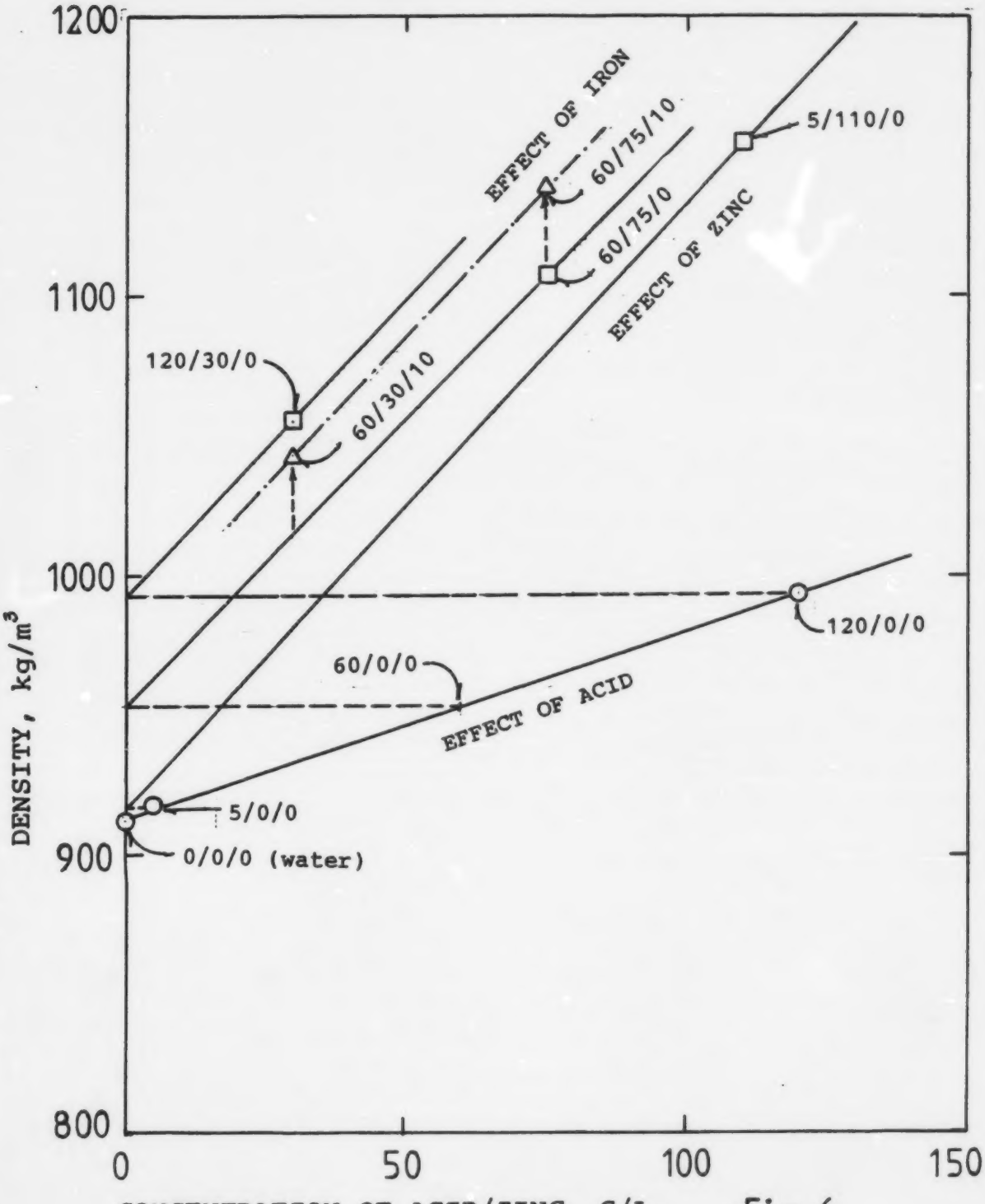

Fig.6

a single equation can be used to express the solution density. It consists of linear increments of density corresponding to the three components:

$$d = d_W + 0.637\ C_A + 2.162\ C_Z + 2.536\ C_I \qquad (5)$$

In the above equation the densities of solution, d, and of water, d_W, are expressed in kg/m^3 and C_A, C_Z and C_I are concentrations of acid, zinc and iron, respectively, in g/L. The maximum error in expressing the data measured using the above equation is 1% with an average error of 0.3%. The density data are considered accurate to $\pm$ 0.2%. Somewhat more accurate equations, one for each temperature utilized, are listed in Appendix B. Because of its simplicity, the single equation is useful for a rapid, approximate estimate of solution density. It is noted that the effect of pressure on density, in the pressure range utilized, is very small.

The equations were derived using a multi-variable least-squares fitting computer program based on the measured density data.

4.5 Oxygen solubility in Cominco autoclave effluent and in a sample containing Lignosol

The oxygen solubility was determined in a zinc-rich acid solution containing 0.3 g/L Lignosol (5/110/1/0.3) at 125°C using partial pressures of pure oxygen of 10,7 and 4 atm and also at 155°C using air at partial pressures of 10,7 and 4 atm. The results at 125°C indicate that the solubilities conform to Henry's law. This is the same result as that

obtained for the other solubility determinations with pure oxygen. Furthermore, the solubility of oxygen in the solution containing Lignosol is essentially identical to that without Lignosol (5/110/1) to within a fraction of a percent, as noted in Table I. It should be mentioned that as part of the experimental procedure, the high pressure absorber is equilibrated for over twelve hours at the high temperatures so that if Lignosol tends to decompose, the equilibrium will be with the Lignosol decomposition products in solution. It appears that whereas the Lignosol decomposition products may have useful surfactant properties, they do not significantly influence the oxygen solubility.

As stated earlier, the degree of uncertainty is greater for the determinations using air as the dissolving gas, because the solubility of air (nitrogen in particular) is considerably lower than that of pure oxygen and because it is necessary to sample a small volume of gas desorbed from the solvent at low pressure and to analyze it using gas chromatography. The results for the solution 5/110/1/0.3 Lignosol at 155°C indicate that Henry's law is obeyed and that only a slightly lower oxygen solubility is obtained from air than that obtained with pure oxygen, both calculated for an oxygen partial pressure of one atm. The result obtained with compressed air is 0.862 (10^{-5}) mole fraction oxygen compared with 0.880 (10^{-5}) for the comparable sample containing no Lignosol and using pure oxygen. The difference is 2.0% reduction which is within experimental error. Thus, it may be concluded that Lignosol has a negligible effect on the solubility of either pure oxygen or oxygen from air when added at a concentration of 0.3 g/L.

The Cominco autoclave effluent sample of May, 1990, contained salts other than zinc and iron and hence, the oxygen solubility results cannot

be compared directly to those for the prepared solutions. It is noted, however, that the density is significantly higher than for all the synthetic solutions, indicating significantly higher concentrations of dissolved salts. There is a definite qualitative inverse relationship between the density of the solution, which is affected by the concentration of dissolved salts, and the oxygen solubility in it. The more dense the solution, the lower the oxygen solubility. Hence, it appears consistent that the high density plant solution with a high concentration of dissolved salts, and a correspondingly high density, has a relatively low solvating power for oxygen. The oxygen solubility was determined using pure oxygen at atmospheric pressure at 50°C and also using compressed air at 155°C. The results are listed in Table III and are shown graphically in Figures 3 and 4. It is concluded that the low oxygen solubility in the plant solution has a profound effect on the oxidation rates of minerals present in the autoclave during pressure leaching.

It is of interest to test the models for density and oxygen solubility with the Cominco plant sample even though the compositions of zinc and iron exceed those for which the equations are applicable. Using Equation 5 for density and assuming that magnesium affects the density in the same way as zinc, the calculated density at 155°C is 1273 kg/m^3 which can be compared with the measured density of 1286 kg/m^3 . Furthermore, if Equation 12 of Appendix B is used, the calculated density is 1280 kg/m^3, a difference of 0.5% from the measured value. The other dissolved components would be expected to increase the calculated density, but their effect is unknown.

Next, the oxygen solubility in a solution having the composition of the Cominco sample can be estimated using Equation 4. Again, if it is assumed that magnesium has the same influence on the solubility as zinc,

TABLE III OXYGEN SOLUBILITY IN A SOLUTION CONTAINING LIGNOSOL AND IN A COMINCO PRESSURE LEACHING AUTOCLAVE EFFLUENT SAMPLE

1. Composition: g/L of Acid/Zinc/Iron/Lignosol 5/110/1/0.3

(a) Temperature: 125°C
Oxygen pressures: 10, 7, 4 atm.

Results with pure oxygen:	s	0.0107
	$(10^5)x$	0.624
	$(10^{-3})H$	160
	β	0.00745

(b) Temperature: 155°C
Oxygen solubility using air pressures of: 10,7,4 atm.

Results with air in absorber:	s	0.0143
	$(10^5)x$	0.862
	$(10^{-3})H$	116
	β	0.0063

2. Cominco pressure leaching autoclave effluent, May, 1990:

(a) Temperature: 50°C
Oxygen pressure: 1 atm.

Results with pure oxygen:	s	0.0073
	$(10^5)x$	0.42
	$(10^{-3})H$	238
	β	0.0051

(b) Temperature: 155°C
Oxygen solubility using air pressures of 10,7,4 atm.

Results with air in absorber:	s	0.0101
	$(10^5)x$	0.627
	$(10^{-3})H$	159
	β	0.0076

Nomenclature as in Table I

then the oxygen solubility corresponding to a partial pressure of one atmosphere is 0.0076 g/L compared to the measured solubility of 0.0101 g/L. On the other hand, if the effects of magnesium, copper and calcium are neglected, the calculated solubility is 0.0088 g/L, a difference of 13% from the measured solubility. Although these models give correct order-of-magnitude results, it is apparent that they cannot be used to accurately predict the solution behavior.

5.0 CONCLUSIONS

5.1 The oxygen solubility in aqueous solutions of sulfuric acid and zinc and iron sulfates is very low; for an oxygen partial pressure of one atmosphere it is of the order of 0.02 g/L or 1 x (10^{-5}) mole fraction oxygen.

5.2 The solubilities of oxygen in aqueous sulfuric acid containing zinc and iron sulfates obey Henry's law.

5.3 There is a minimum solubility of oxygen in water and in aqueous solutions of sulfuric acid and zinc and iron sulfates at a temperature of about 95°C.

5.4 There is a dramatic decrease in oxygen solubility as the zinc content and/or iron content and/or acid content of the solution increases.

5.5 A two-stage process can be successfully utilized to measure the solubilities of oxygen in aqueous solutions first by saturation batch-wise at high pressure and then by quantitative desorption and expansion of the gas through a needle valve at low pressure using a flow process.

5.6 There is a systematic increase in the solution density as the sulfuric acid content and/or zinc sulfate content and/or iron sulfate content of the aqueous acid salt solutions is increased.

6.0 REFERENCES

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7.0 APPENDIX A

Vapor pressures of aqueous sulfuric acid, zinc and iron sulfate solutions

Raoult's law is sometimes used to estimate an 'ideal' vapor pressure resulting from the dissolution of a non-volatile solute such as a salt in a volatile solvent:

$$p = x_s P^\circ = (1 - x_1) P^\circ \qquad (6)$$

In the above equation p is the vapor pressure of the solution in which x_s is the mole fraction solvent, x_1 is the mole fraction solute and P° is the pure solvent vapor pressure. Most often the vapor pressure is not ideal and is expressed by means of an activity coefficient, :

$$p = (1 - \gamma_1 x_1) P^\circ \qquad (7)$$

For two dissolved, non-volatile components, the equation for partial pressure is written as:

$$p = (1 - \gamma_1 x_1 - \gamma_2 x_2) P^\circ \qquad (8)$$

The reduction in vapor pressures as a result of the dissolved, non-volatile solutes is then:

$$\Delta p = (- \gamma_1 x_1 - \gamma_2 x_2) P^\circ \qquad (9)$$

In the current experiments, the vapor pressures of aqueous sulfuric acid solutions, available in the literature (Chemical Engineers' Handbook, Perry and Green, 1984) are taken as the solvent vapor pressure, P°. The activity coefficients γ_1 and γ_2 have been calculated as 0.692 and 0.819 for zinc and iron salts, respectively, for a temperature of 100°C from data given in the Handbook of Chemistry and Physics (Weast, 1989). For lack of additional data at higher temperatures, it has been assumed that the activity coefficients remain the same at the higher temperatures used in this work. The calculated vapor pressures are listed in Table IV for the solutions used in this work.

TABLE IV Vapor pressures of aqueous solutions of sulfuric acid, zinc and iron sulfate salts

Solution		95°C	125°C	155°C	185°C
water	atm	0.8342	2.270	5.329	10.05
	psi	12.26	33.37	78.34	160.9
60 g/L acid	atm	0.8057	2.190	5.101	10.04
	psi	11.84	32.19	74.98	147.6
120 g/L acid	atm	0.7791	2.116	4.888	9.19
	psi	11.45	31.10	71.86	135.1
120 g/L acid, 30 g/L Zn	atm	0.7741	2.102	4.857	8.068
	psi	11.38	30.90	71.40	134.2
60 g/L acid, 75 g/L Zn	atm	0.7946	2.160	5.033	8.340
	psi	11.68	31.76	73.99	145.5
60 g/L acid, 30 g/L Zn, 10 g/L Fe	atm	0.7986	2.171	5.057	8.374
	psi	11.74	31.92	74.34	146.3
60 g/L acid, 75 g/L Zn, 10 g/L Fe	atm	0.7918	2.152	5.014	8.306
	psi	11.64	31.64	73.70	145.1
5 g/L acid, 110g/L Zn, 1 g/L Fe	atm	0.7973	2.210	5.185	8.565
	psi	11.2	31.49	76.22	157.1

8.0 APPENDIX B

Solution densities

Equations obtained expressing solution density as a function of acid, zinc and iron concentrations are as follows:

At 95°C:

$$d = 963.5 + 0.634\ C_A + 2.255\ C_Z + 2.475\ C_I \quad (10)$$

R = Correlation Coeff. = 0.9995

At 125°C:

$$d = 940.5 + 0.621\ C_A + 2.183\ C_Z + 2.485\ C_I \quad (11)$$

R = 0.9995

At 155°C:

$$d = 916.0 + 0.623\ C_A + 2.132\ C_Z + 2.590\ C_I \quad (12)$$

R = 0.999

At 185°C:

$$d = 883.8 + 0.671\ C_A + 2.078\ C_Z + 2.594\ C_I \quad (13)$$

R = 0.9994

It is noted that in this case the first constant in the above equations does not correspond exactly to the density of water. The density, d, is in kg/m^3 and C_A , C_Z and C_I are in g/L of acid, zinc and iron, respectively.

9.0 APPENDIX C

Analysis of Cominco autoclave effluent sample

Sample date: May 28, 1990

Source of sample: Cominco autoclave effluent, after 6 - 8% water loss because of flashing during sampling.

Components:		
	Zinc	145 g/L
	Iron 2+	5.9 g/L
	Free acid	32.3 g/L
	Magnesium	9.1 g/L
	Lignosol	0.6 g/L (0.3 g/kg conc.)
	Calcium	380 mg/L
	Copper	935 mg/L

Analysis as determined by Cominco laboratory.

Normal additional components not specified in the essay:

Manganese	1.5 to 2.0 g/L
Cadmium	0.5 g/L

10.0 APPENDIX D

Equations used for calculating solubility

The oxygen solubility at high pressure is made up of two parts: the amount of oxygen released at atmospheric pressure and 50°C and the amount of oxygen still dissolved in the solvent at atmospheric pressure and 50°C:

$$X = p\,(x_{50} + x_T) \qquad (14)$$

X is the mole fraction of oxygen at the high pressure of oxygen, p*, atm and a temperature T, K

x_{50} is the mole fraction solubility of oxygen (separately determined) at an oxygen pressure of one atm and 50°C

p is the partial pressure of oxygen in the desorbed gas, atm

x_T is the number of moles of oxygen released in the desorber per mole of solvent for an oxygen pressure of one atm

$$x_T = 1000\,B/(R\,T\,m) \qquad (15)$$

B is the ratio of the volume of gas released in the desorber to the volume of solvent collected

R is the gas constant, 82.05 cm^3atm/mole K

T is the temperature in the desorber, 323.15 K

m is the molar concentration of solvent at high temperature, T, mol/L

$$x = X/p^* \tag{16}$$

x is the mole fraction oxygen at high pressure corresponding to a partial pressure of one atm

p^* is the partial pressure of oxygen in the high pressure absorber, atm

$$H = 1/x \tag{17}$$

H is Henry's constant, atm/mole fraction

$$s = 32.0\ (m)\ x \tag{18}$$

s is the solubility in g/L for an oxygen pressure of one atm

$$\beta = 22.414\ (m)\ x \tag{19}$$

β is the Bunsen coefficient, cm^3 oxygen at STP per cm^3 solvent